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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/EP93/02059 (22) International Filing Date: 31 July 1993 (31.07.93) (30) Priority data: 9216767.5 7 August 1992 (07.08.92) GB (71) Applicant (for AU BB CA GB IE LK MN MW NZ SD only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). (71) Applicant (for all designated States except AU BB CA GB IE LK MN MW NZ SD): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). (72) Inventor: SHANA'A, May ; 17 Gardens Road, Bebington, Wirral, Merseyside L63 7QZ (GB).		(74) Agent: ELLIOTT, Peter, William; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB). (81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: WASHING COMPOSITION (57) Abstract <p>The present invention relates to the washing composition. More particularly, the invention relates to compositions for washing the human body which deliver oily components to the skin or hair. We have now determined that, foaming, mild washing compositions having an oily skin benefit can be formulated with: (a) an oily component; (b) one or more nonionic sugar-based surfactant, said surfactant being present in weight excess over the oily component, and; (c) a water soluble cationic polymer. Generally, the sugar based nonionic is selected from the group comprising aldonamides, alkylpolyglycosides and mixtures thereof.</p>		

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WASHING COMPOSITION

- 5 The present invention relates to washing compositions. More particularly, the invention relates to compositions for washing the human body which deliver oily components to the skin or hair.
- 10 It is well known to add oil to bath water so as to obtain a so-called skin benefit. It is also known to prepare compositions which contain both one or more oils and a surfactant so as to form an emulsion on dilution with water.
- 15 EP 0366070 discloses bathing compositions comprising an oily component (preferably a silicone oil, jojoba or olive oil, 2-ethyl hexanoic acid, squalene or cetyl octanoate), a non-ionic surfactant (preferably a poly-oxyethylene alkyl ether) and a cationic polymer (preferably synthetic N,N-dimethyl-
- 20 3,5-methylenepiperidinium chloride polymer or distearyl-dimethyl-ammonium chloride polymer). The compositions are generally pressed into a tablet so as to provide a convenient dosage form. In that document, it is said that the oily component forms an emulsion in water in the
- 25 presence of the non-ionic surfactant and that the cationic polymer exerts a synergistic effect with the aforementioned emulsion to improve the texture of the skin and to suppressing dryness after bathing. The oil content of the bath water disclosed in EP 0366070 ranges from 2 to 500ppm,
- 30 and the surfactant content of the product is such that it preferably ranges from 18-60wt% of the oil content, that is, the surfactant content is always less than the oil content so as to avoid foaming.

- 2 -

The above-mentioned compositions have a skin benefit but do not clean well due to the low level of surfactant present. Moreover, while the presence of foam is undesirable in moisturising bathing compositions, many consumers require bathing or other washing compositions to foam. It is known that oils have a depressant effect on foam, eg. in fabric washing compositions silicone oils are used as antifoams as disclosed in US 3843558 and GB 1407997. Other oils are also known as antifoams.

In addition, it is important that washing compositions are mild to the skin. While non-ionic surfactants are known to be particularly mild, especially as compared with anionic and cationic surfactants, non-ionic surfactants generally exhibit much worse foaming performance than ionic surfactants.

From the above, having regard to the poor foaming properties of non-ionic surfactants and the anti-foam effects of oils, it can be seen that the preparation of a foaming, mild washing composition capable of depositing an oil on the skin presents considerable technical problems.

We have now determined that, foaming, mild washing compositions having an oily skin benefit can be formulated with:

- a) An oily component
- b) At least one non-ionic sugar-based surfactant, said surfactant being present in weight excess over the oily component, and,
- c) A water-soluble cationic polymer.

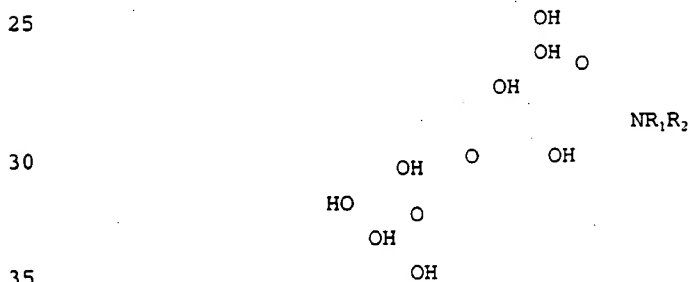
- 3 -

Suitable sugar based surfactants are selected from the group comprising the sugar-amides, sugar-ethers and sugar-esters having surfactant properties.

- 5 Generally, the sugar based non-ionic is selected from the group comprising aldonamides, alkylpolyglycosides and mixtures thereof.

10 Aldonamides are amides of aldonic acid. Aldonic acids are sugar substances (eg. cyclic sugars) in which the aldehyde group (generally found at the C₁ position on the sugar) is replaced by a carboxylic acid. Aldonamides can be based on sugars comprising one saccharide unit, (eg. gluconamide),
 15 two saccharide units, (eg. lactobionamide or maltobionamide) or can be based on longer polysaccharides with an available terminal aldehyde group. Aldonamides are disclosed as emulsifiers in Walden, US 2752334, and as components for use in detergent compositions in our co-pending application US
 20 07/816419.

A specific example of an aldobionamide which may be used for purposes of the invention is the disaccharide lactobionamide set forth below:



wherein R₁ and R₂ are the same or different and are selected from the group consisting of hydrogen; an aliphatic

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hydrocarbon radical (eg., alkyl groups and alkene groups which groups may contain heteroatoms such as N, O or S or alkoxyated alkyl chains such as ethoxyated or propoxyated alkyl groups), preferably an alkyl group having 8 to 24, preferably 10 to 18 carbons; an aromatic radical (including substituted or unsubstituted aryl groups and arenes); a cycloaliphatic radical; an amino acid ester, ether amines and mixtures thereof, except that R₁ and R₂ cannot be hydrogen at the same time, and must have a total carbon chain length of at least 8 on average.

Suitable aliphatic hydrocarbon radicals include saturated and unsaturated radicals including but not limited to methyl, ethyl, amyl, hexyl, heptyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, and allyl, undecenyl, oleyl, linoleyl, linolenyl, propenyl, and heptenyl.

Aromatic radicals are exemplified, for example, by benzyl.

Suitable mixed aliphatic aromatic radicals are exemplified by benzyl, phenyl ethyl, and vinyl benzyl.

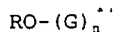
Cycloaliphatic radicals are exemplified by cyclopentyl and cyclohexyl.

Alkylpolyglycosides (APG's) are known for inclusion in hair care and washing compositions, and have the advantages that they are mild, readily biodegradable and preparable from renewable resources.

The alkyl polyglycoside (APG) may be any APG which is capable of being employed in a body or hair care composition. Typically, the APG is one which comprises an alkyl group connected (optionally via a bridging group) to a

- 5 -

block of one or more glycosyl groups. Preferred APG's are described by the following formula:



5

wherein R is a branched or straight chain alkyl group which may be saturated or unsaturated and G is a saccharide group.

10

R may represent a mean alkyl chain length of from about C_5 to about C_{20} . Preferably, R represents a mean alkyl chain length of from about C_9 to about C_{12} . Most preferably the value of R lies between about 9.5 and about 10.5. G may be selected from C_5 or C_6 monosaccharide residues or mixtures of C_5 and C_6 monosaccharide residues, and is preferably a glucoside. G may be selected from the group comprising glucose, xylose, lactose, fructose, mannose and derivatives thereof. Preferably G is glucose.

15

20

The degree of polymerisation, n, may have a value of from about 1 to about 10 or more. Preferably, the value of n lies in the range of from about 1.1 to about 2. Most preferably the value of n lies in the range of from about 1.3 to about 1.5.

25

Suitable alkyl polyglycosides for use in the invention are commercially available and include for example those materials identified by the trademarks: Oramix NS10 ex Seppic; APG225, APG300, APG350, APG550 and APG600 ex Henkel; BW 2762ZA, BW 2762ZB, BW 2761ZA and BW 2761ZB ex Huls; SCS 1050 and SCS 1087 ex ICI.

30

Typically, the water soluble cationic polymer has a cationic charge density (as defined in US patent 3580853) greater than 0.0001 in aqueous solution.

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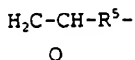
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Cationic charge density refers to the ratio of the number of positive charges on a monomeric unit of which the polymer is comprised to the molecular weight of said monomeric unit.

5 The preferred cationic polymer for use in the washing composition of the invention is a cationically substituted galactomannan gum. The gum occurs naturally as guar gum, the principal component of the seed of the guar plant, cyamopsis tetragonolobus. The guar molecule is essentially
10 a straight chain mannan branched at quite regular intervals with single membered galactose units on alternative mannose units. The mannose units are linked to each other by means of beta (1-4) glycosidic linkages. The galactose branching is accomplished through an alpha (1-6) linkage. The
15 cationic derivatives are obtained by reaction between the hydroxyl groups of the polygalactomannan and reactive quaternary ammonium compounds. The degree of substitution of the cationic groups is sufficient to provide a cationic charge density of 0.0001 to 0.0017. The quaternary ammonium
20 compounds which can be used for preparing the cationic agents employed in this invention are those of the general formula



where R^1 , R^2 and R^3 are methyl or ethyl groups and R^4 is an
35 epoxyalkyl group of the formula



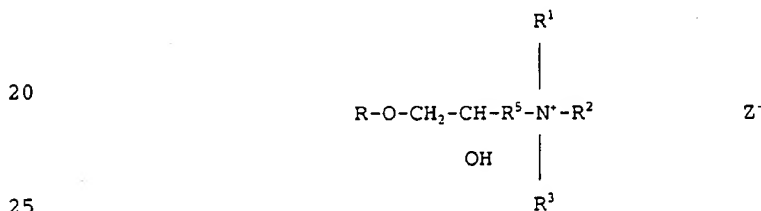
- 7 -

or halohydrin group of the formula



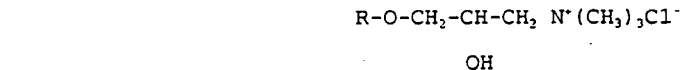
where R^5 is a C1-C3 alkylene group and X is chlorine or bromine, Z being an anion such as Cl^- , Br^- , I^- or HSO_4^-

These reagents would lead to the formation of a galactomannan derivative of the formula



where R represents guar gum.

An example of a suitable quaternary ammonium derivative is hydroxypropyltrimethylammonium guar gum of the formula



Such a material is available commercially from Celanese-Stein Hall, USA under the name JAGUAR C-13-S; the word JAGUAR is a trade mark. This material also has the CTFA designation Guar Hydroxypropyltrimonium Chloride. JAGUAR C-13-S has a cationic charge density of 0.0008. Another

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suitable material is that known as JAGUAR C-17 which is similar to JAGUAR C-13-S but has a higher degree of substitution of cationic groups and has a cationic charge density of 0.0016. A further example of a suitable guar derivative is the hydroxypropylated cationic guar derivative known as Jaguar C-16 which as well as containing the above cationic quaternary ammonium groups also contains hydroxypropyl ($-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$) substituent groups. JAGUAR C-16 has a cationic charge density of approximately 0.0008, the degree of substitution of the hydroxypropyl groups being 0.8 - 1.1.

The preferred oily components are selected from natural fats and oils, preferably di glycerides having a carbon number of 24-44 and tri-glycerides having a carbon number of 30-73, more preferably, olive oil, coconut oil, and/or cacao fats: hydro-carbons, preferably liquid paraffin and/or vaseline: higher fatty acids, preferably having a branched or straight, saturated or unsaturated carbon chain length of C_{12} - C_{22} : higher alcohols, preferably lauryl, cetyl, stearyl, oleyl alcohols, cholesterol, and/or 2-hexyldecanol: esters, particularly isopropyl esters, preferably isopropyl myristate and/or palmitate: silicone oils, preferably dimethicone, phenyl dimethicone, dimethicone copolyol, and/or cyclomethicone.

The most preferred oil components are olive oil, the silicone oils, the isopropyl esters and liquid paraffin.

In addition to the above, compositions according to the present invention can comprise a polyol, preferably glycerol.

Minor components are inessential but typical components of washing compositions. These can be selected from one or

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more of opacifiers, preferably 0.2-2.0%wt; preservatives, preferably 0.2-2.0%wt and perfumes, preferably 0.5-2.0 wt%. Optional components include colouring agents, germicides, anti-oxidants and preservatives.

5

In embodiments of the invention, typical compositions comprise (on product):

10

- a) 1 to about 50wt% oily component,
- b) about 1 to 50wt% non-ionic sugar based surfactant, said surfactant being present in weight excess over the oily component (a), and,
- c) 0.001-2wt% water soluble cationic polymer.

15

20

Preferred levels of oily component fall in the range 3-20wt% on product, more preferably 4-10wt%. Preferred levels of non-ionic sugar based surfactant fall in the range 10-30wt% on product. The preferred ratio of the oily component to the sugar based non-ionic surfactant falls in the range 1:1.5-1:6, higher ratios being preferred for concentrated products, typical ratios for non-concentrates being 1:1.5 to 1:4.

25

Particularly preferred embodiments of the invention comprise:

30

- a) 4-10wt% of a silicone oil,
- b) 10-20wt% of a non-ionic surfactant selected from lactobionamide, alkylpolyglycoside or mixtures thereof, and,

- 10 -

- c) 0.01-1wt% of hydroxy propyl trimethyl ammonium guar gum.

5 In order that the present invention can be further understood it will be described hereinafter with reference to examples.

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EXAMPLES:

In the examples given below the following components are identified by their trade names:

5

ORAMIX NS-10

An alkylpolyglucoside,
available in the marketplace
from SEPPIC.

10

APG-600
(PLANTAREN)

An alkylpolyglucoside,
available in the marketplace
from HENKEL.

15

C12-LACTOBIONAMIDE

An aldonamide as described
above having R1 = hydrogen and
R2 = lauryl residue.
Manufactured according to US
07/816419.

20

C14-LACTOBIONAMIDE

An aldonamide as described
above having R1 = hydrogen and
R2 = myristyl residue.
Manufactured according to US
07/816419.

25

COCO-LACTOBIONAMIDE

An aldonamide as described
above having R1 = hydrogen and
R2 being derived from the
fatty acids of coconut (Cocos
nuctifera) fat (predominantly
C₁₂). Manufactured according
to US 07/816419.

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	Brij 76	Alcohol ethoxylate (C18, EO average 10), non-ionic surfactant as supplied by ATLAS.
5	Genapol 0-020	Alcohol ethoxylate (C18 EO average 2), non-ionic surfactant as supplied by HOECHST.
10	BC89/138 (silicone)	A silicone oil available as an emulsion (containing 50%wt silicone) from the Basildon Chemical Company Ltd.
15	JAGUAR C13-S	Guar hydroxy propyl tri-methyl ammonium chloride available in the marketplace from Celanese-Stein Hall.
20		

EXAMPLES 1-6 and Comparative Examples

25 Compositions were prepared with formulations as given in table 1 below. The JAGUAR C13-S was made up into a 2wt% solution from powder, all other components were used as supplied in the quantities given.

TABLE 1

Sample Ingredients	1	2	3	4	5	6	7	8	9	10
Oramix (52%)	20	10	10	20	40	-	-	-	-	-
APG 600 (50%)	-	10	-	-	-	-	-	-	-	-
C ₁₂ Lactobionamide	10	10	10	-	-	20	-	-	-	-
C ₁₄ Lactobionamide	-	-	5	-	-	-	-	-	-	-
Coco Lactobionamide	-	-	-	10	-	-	-	-	-	-
Brij 76	-	-	-	-	-	-	20	-	-	-
Genapol 0-20	-	-	-	-	-	-	-	20	20	20
Glycerol	10	10	10	10	10	10	10	10	10	10
Silicone (50%)	10	10	10	10	10	10	10	10	-	10
Jaguar C ₁₃₋₅ (2%)	5	5	5	5	5	5	-	-	-	5
Sorbic acid	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37
Na ₃ citrate	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37
Perfume	1.00	1.0	2.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Foam	80	70	107	91	109	-	9	0.5	2	1.5
Deposition	0.67	0.28	0.36	0.26	0.50	-	0.30	9	-	1.2

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Compositions were prepared by adding the actives to water, under shear, followed by addition of the oil, any glycerol, and polymer, preservatives and perfume in sequence. Mixing was performed at room temperature.

5

Foam values given in Table 1 are foam heights in cm using a cylinder shaking method. In the 'cylinder-shaking' test method, 0.25 ml of product was introduced into 50mls of water in a 200ml stoppered measuring cylinder and shaken vigorously 30 times by hand. Each shake involved a vertical up/down motion of 30cm and, on average, twenty shakes occurred every 5 seconds. After shaking the stoppers were removed and the initial foam height was measured.

15

Examples 1-6 of the present invention and comparative examples 7-10 show that typical foam volumes of 1.5-9.0 (expressed in terms of foam height) are obtained with formulations comprising conventional non-ionics (examples 7-9) even when very high levels of ethoxylation are used (compare 7 with 8-10). For a particular non-ionic (see examples 8-10), foam volumes are particularly bad in the presence of silicone oil (compare examples 8: 0.5 with oil and 9: 2 without oil). The limits of error in these examples are around 1 unit.

25

Example 6 which contained C₁₂ lactobionamide as the sole surfactant component is an example of a solid formulation.

30

Examples 1-5 exhibit much higher foam volumes in the presence of oil, than comparable formulations (examples 7, 8 and 10, with conventional non-ionics) in the presence of oil. This illustrates how formulations based on conventional non-ionic surfactants, would not achieve the benefit of the present invention in terms of foam volume. It is believed that this is due to the foam-breaking effects

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- 15 -

of oil on surfactant systems as well as the relatively poor foaming behaviour of non-ionics.

5 Silicone deposition was measured using X-ray fluorescence in arbitrary units. It can be seen from the results that all of the compositions deposit at least 0.26 units of silicone which is a satisfactory level of deposition. While the conventional non-ionic formulations of comparative examples 8 and 10 exhibit high levels of silicone deposition, they do
10 not have acceptable foam behaviour as discussed above.

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CLAIMS:

1. Foaming, mild washing compositions comprising:
 - 5 a) An oily component,
 - b) One or more non-ionic sugar-based surfactant, said surfactant being present in weight excess over the oily component, and,
 - 10 c) A water soluble cationic polymer.
2. Composition according to claim 1 wherein the sugar based non-ionic is selected from the group comprising
15 aldonamides, alkylpolyglycosides and mixtures thereof.
3. Composition according to claim 1 wherein the water soluble cationic polymer has a cationic charge density greater than 0.0001 in aqueous solution.
20
4. Composition according to claim 1 wherein the oily component is selected from:
 - 25 a) natural fats and oils, preferably di glycerides having a carbon number of 24-44 and tri-glycerides having a carbon number of 30-73, more preferably, olive oil, coconut oil, and/or cacao fats and/or,
 - b) hydro-carbons, preferably liquid paraffin and/or
30 vaseline and/or,
 - c) higher fatty acids, preferably having a branched or straight, saturated or unsaturated carbon chain length of C_{12} - C_{24} and/or,
 - 35

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d) higher alcohols, preferably lauryl, cetyl, stearyl, oleyl alcohols, cholesterol, and/or 2-hexyldecanol: esters, particularly isopropyl esters, preferably isopropyl myristate and/or palmitate and/or,

e) silicone oils, preferably dimethicone, phenyl dimethicone, dimethicone copolyol, and/or cyclomethicone.

5. Composition according to claim 1 further comprising a polyol, preferably glycerol.

6. Composition according to claim 1 comprising:

a) 1 to about 50wt% oily component,

b) about 1 to 50wt% non-ionic sugar based surfactant, said surfactant being present in weight excess over the oily component (a), and,

c) 0.001-2wt% water soluble cationic polymer.

7. Composition according to claim 6 wherein the ratio of the oily component to the sugar based non-ionic surfactant falls in the range 1:1.5-1:6.

8. Composition according to claim 6 comprising:

a) 4-10wt% of a silicone oil,

b) 10-20wt% of a non-ionic surfactant selected from lactobionamide, alkylpolyglycoside or mixtures thereof, and,

- 18 -

- c) 0.01-1wt% of hydroxy propyl trimethyl ammonium guar gum.

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/EP 93/02059

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 A61K7/50 A61K7/06 A61K7/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 531 650 (GOLDWELL AKTIENGESELLSCHAFT) 17 March 1993 see page 1 - page 4 see claims 1,2,4,6,10 ---	1,2,4,5, 7
X	EP,A,0 463 780 (UNILEVER PLC) 2 January 1992 see the whole document ---	1-4,6,8
X	EP,A,0 398 177 (KAO CORPORATION) 22 November 1990 see the whole document ---	1,2,4-6, 8
X	US,A,5 085 857 (E. S. REID) 4 February 1992 see column 1 - column 5, line 20 see claims 1,5,6,8-10 ---	1-8
-/--		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

20 December 1993

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Name and mailing address of the ISA

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 400 976 (UNILEVER PLC) 5 December 1990 see the whole document ---	1-4,6-8
A	WO,A,92 05764 (THE PROCTER & GAMBLE COMPANY) 16 April 1992 see the whole document ---	1-8
A	FR,A,2 523 962 (CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE) 30 September 1983 see the whole document -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 93/02059

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		US-A- 5152914	06-10-92
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		CA-A- 2092191	29-03-92
		CN-A- 1061150	20-05-92
		EP-A- 0550656	14-07-93
FR-A-2523962	30-09-83	NONE	